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Multidimensional effects in dissociative chemisorption: H₂ on Cu and Ni surfaces

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It is shown that, in order to describe and understand the trends found experimentally for the variation of the H₂ sticking probability with crystal face on Cu and Ni surfaces, the dynamics of all six molecular degrees of freedom must be included. The effective-medium theory is used to estimate the multidimensional interaction potential and the dynamics is studied using two- and six-dimensional quantum and classical simulations.

The dissociation of a molecule at a surface is a very complex dynamical process involving many degrees of freedom. Upon approach to the surface the molecule vibrates and rotates, and during the dissociation process some or all of the energy in these degrees of freedom is transferred into translational energy of the atoms relative to each other. The surface degrees of freedom, phonons, and electron-hole pair excitations also play a role. The usual approach to describe such a process has been to reduce the problem to only include the most essential coordinates. The earliest attempt by Lennard-Jones¹ reduced the problem to an essentially one-dimensional one. The Lennard-Jones picture is still widely used and very useful for qualitative considerations. More recently, classical and combined classical and quantum-mechanical simulations including all the molecular degrees of freedom have been carried out,² but because of the difficulty in obtaining an interaction potential for all the molecular degrees of freedom, because quantum simulations cannot presently be carried out for all the molecular degrees of freedom simultaneously, and in order to attempt to single out the most important aspects of the process, low-dimensional models have emerged as the most popular approach.³⁻⁵ Two-dimensional model calculations have, for instance, been extremely useful in describing and interpreting the role of vibrational excitations for H₂ dissociation over Cu surfaces.^{4,5}

In the present paper we will consider H₂ dissociation on various Cu and Ni surfaces. We show that a description of the dynamics of all six molecular degrees of freedom is necessary in order to understand the trends in reactivity from one crystal face to the next on these metals.

Molecular-beam experiments have shown that the open (110) surface of Ni dissociates H₂ with high probability at low translational energy of the incoming molecule, indicating nonactivated dissociation.⁶ On Ni(111) the dissociation probability is essentially zero at low translational energy and increases with kinetic energy, indicating activated dissociation.⁶ On Cu surfaces the picture is quite different. Here the dissociation of H₂ is activated on all surfaces, and the sticking coefficients on the (110) and

(111) surfaces are very similar.⁷

In the present work we use a model potential based on the effective-medium theory⁹ to get the full six molecular degrees of freedom (6D) potential energy surface on the (111) and (110) surfaces of both Cu and Ni by only changing the input parameters characterizing a given surface (*d*-band positions, band widths, work functions, etc.). The dissociation dynamics is first simulated quantum mechanically and quasiclassically (including the vibrational zero-point motion of the molecule) in two dimensions, including only the center-of-mass motion of the molecule perpendicular to the surface and the H-H distance. This shows that the quasiclassical method gives a reasonable representation of the full quantum dynamics for this potential and it can therefore be used to investigate the effects of taking all six molecular degrees of freedom into account. We find that even though the *minimum* barrier to dissociation is smallest on the (110) faces of *both* Cu and Ni this only shows up as a qualitatively different sticking behavior for the Ni faces, whereas for Cu the sticking probabilities on the two faces are quite similar. The reason is that the difference in minimum barrier height is compensated (rather fortuitously) by different multidimensional properties of the potential energy surface and effects of the full-dimensional H₂ dynamics on the two Cu surfaces.

The effective-medium potential is approximate and not intended to describe the absolute magnitude of energy barriers to a very high precision. It has the advantage that the role of the molecular resonances and the metal *d* band and their degree of filling is explicitly taken into account¹⁰ and that it includes adsorbate-metal and metal-metal interactions in a realistic way.¹¹ The details of the effective-medium potential for H₂ on Cu and Ni surfaces can be found in Ref. 9. The method is based on density-functional theory and most of the parameters entering the potential are calculated directly from self-consistent solutions for H, H₂, Cu, and Ni embedded in a homogeneous electron gas or determined from calculations or experiments for the clean metal surfaces. The potential contains a single fitting parameter describing

the strength of the adsorbate—the metal-*d* hopping matrix element. This has been fixed to give the correct difference in the atomic hydrogen chemisorption energies on Cu and Ni. With no further adjustments the potential gives reasonable results for the H₂-Cu, Ni systems: Dissociative adsorption on Cu is activated, on Ni it is nonactivated or with a small barrier, and on both metals the (111) face is found to have a larger barrier than the (110) surface. The calculated barrier for H₂ on Cu is of the order 0.2 eV which is too small compared to the experimental one, which is believed to be of the order 0.7 eV.^{8,12}

For the present purposes we have changed one additional parameter¹³ to increase the barriers for H₂ on Cu to more realistic values of the order 0.5 eV. This does not change any of the trends discussed above.¹⁴ No attempt has been made to adjust the parameters to exactly reproduce the experimental sticking probabilities. The important point of the present work is to study the *trends* from one metal to the next and from one face to the next, and for that purpose the effective-medium potential is well suited because it does not involve any new fitting when the metal or face is changed.

The quantum dynamics is simulated by numerical solution of the time-dependent Schrödinger equation using the split-operator algorithm of Feit, Fleck, and Steiger.¹⁵ In the quasiclassical simulations, for each energy, 200 trajectories are calculated by integration of Newton's equations of motion. The initial vibrational energy is chosen to be equal to the ground-state vibrational energy of the free molecule. The initial vibrational phase and, in 6D, the orientation of the molecule and the impact parameter, are selected at random.¹⁶ In both the quantum and the classical calculations the sticking probability has been taken to be equal to the probability of passing the barrier to a local minimum configuration.

In Fig. 1 we first establish that the quantum and quasiclassical simulations give similar results in two dimensions. The agreement is best for molecules approaching

the surface in the vibrational ground state, but even for the excited states it is reasonable.¹⁶ The results are in qualitative agreement with similar comparisons in the literature^{17,4} but, in particular for Cu, the agreement between the quantum and classical results in the present case is better due to differences in the potentials used.¹⁶ It should be pointed out that the quasiclassical results are only used for comparing trends and not, for instance, to quantitatively study the very small sticking probabilities at low energies. The potential cuts used in the two-dimensional (2D) simulations are shown in Fig. 2, where the differences between Ni and Cu are clearly illustrated.

Having established that for the present potential energy surface a quasiclassical simulation gives very reasonable results we use the quasiclassical dynamics to calculate the sticking probability including all six degrees of freedom of the molecule. The results are shown in Fig. 3. For the two Ni surfaces the change in sticking probability vs translational energy [*S*(*E*)] is minor. The same is true for Cu(111) whereas for Cu(110) there is a dramatic change. Indeed, for the 6D simulations the *S*(*E*) functions for Cu(111) and (110) are very similar whereas the 2D functions are very different. This is true both for molecules in the vibrational ground state and for molecules in the first excited state.¹⁶ This means that even though the experimental sticking probability is a convolution of sticking of molecules in different vibrationally excited states, we only need to discuss the ground-state results in the following in order to understand the trends.

The large difference between Cu(111) and Cu(110) in the effect of going from two dimensions to 6D has two main origins. The most important is that the barrier for dissociation varies much more drastically with impact parameter on the (110) surface than on the (111) surface. This is illustrated in Fig. 4 which shows the distribution of activation barriers over the surface unit cell for the four surfaces studied. Clearly the rough Cu(110) surface

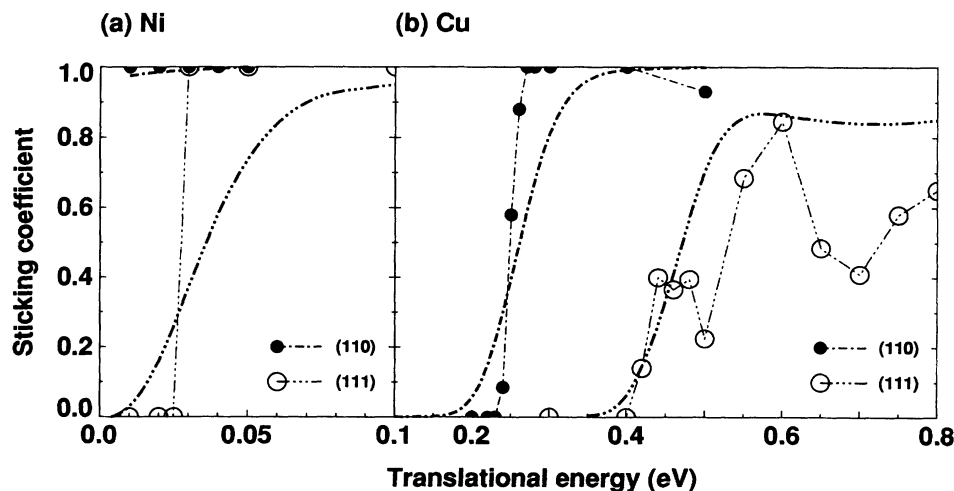


FIG. 1. Comparison of the quantum (thick, smooth curves) and quasiclassical (thin, broken curves; data points) calculations of the sticking coefficient of H₂ on the (110) and (111) surfaces of Cu and Ni. The dynamics is described for the center-of-mass motion of the molecule perpendicular to the surface and the H-H distance. The molecule approaches parallel to the surface. Figure 2 shows the 2D potentials used in the simulations and also includes a sketch of the dissociation geometry chosen.

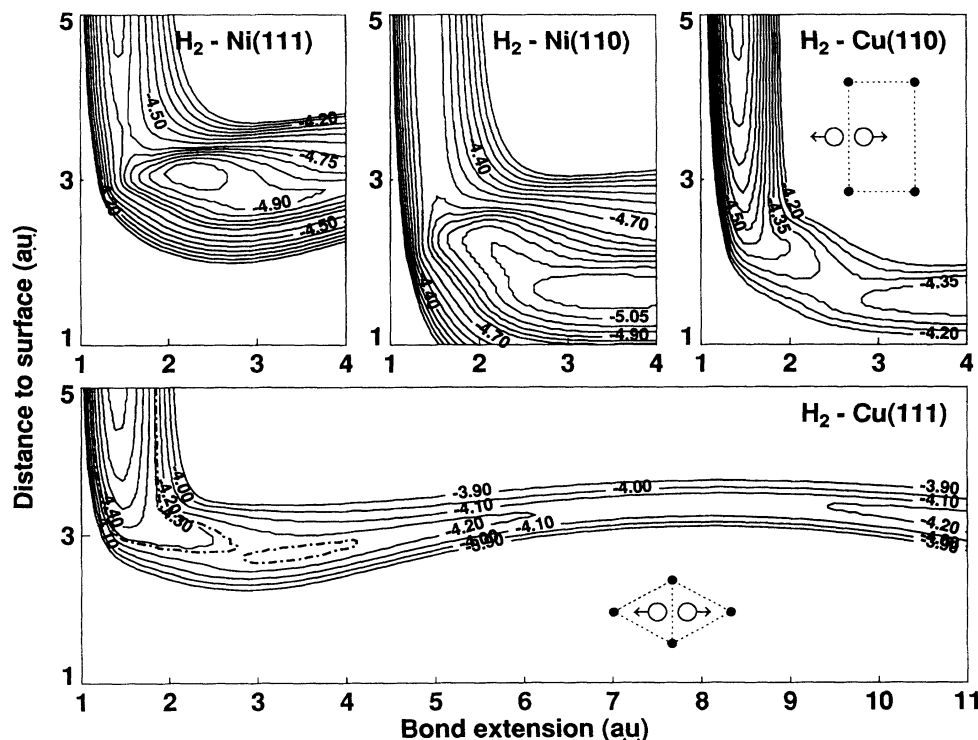


FIG. 2. Contour plot of the H_2 -metal potential outside the (111) and (110) surfaces of Cu and Ni. The dashed contour is included to indicate that there is a local minimum for a bond extension of about 3 a.u. on Cu(111). The potential is shown in a plane perpendicular to the surface in the geometries indicated by the insets.

shows substantially larger variations than the smoother (111) surface. Dissociation turns out (in the potential used here) to be easiest inside the troughs of the (110) surface and most difficult along or perpendicular to the close-packed ridges, i.e., the azimuthal orientation is crucial on this face. On the close-packed Cu(111) surface the distribution of barriers is naturally much narrower and therefore does not add significantly to the form of the $S(E)$ curve.

The cut studied in the 2D simulations for Cu(110) (Figs. 1 and 2) thus represents one of the lowest barriers (not necessarily the minimum one), but not a typical one. Had we chosen another cut for the 2D simulation the energy scale for the $S(E)$ function would have changed, but we would not have been able to get the slowly rising $S(E)$ function of Fig. 3.

The other main factor contributing to the reduced difference between Cu(111) and (110) in 6D is that on Cu(111) the 6D simulation opens up for paths that are not accessible in the more confined 2D simulations. The late part of the barrier for Cu(111) in Fig. 2 can be thought of essentially as a barrier for H diffusion on the surface and if the atoms are free to choose paths avoiding positions close to the on-top sites where the barrier is largest, this can lower the effective barrier.

Apart from the effect of variations of the barrier with impact parameter discussed above, the 6D simulations tend to give smaller sticking probabilities than the 2D ones due to variations in barrier height with the polar angle of the incoming molecule. Molecules oriented parallel to the surface, as those studied in the 2D simulations, generally have a larger probability of dissociat-

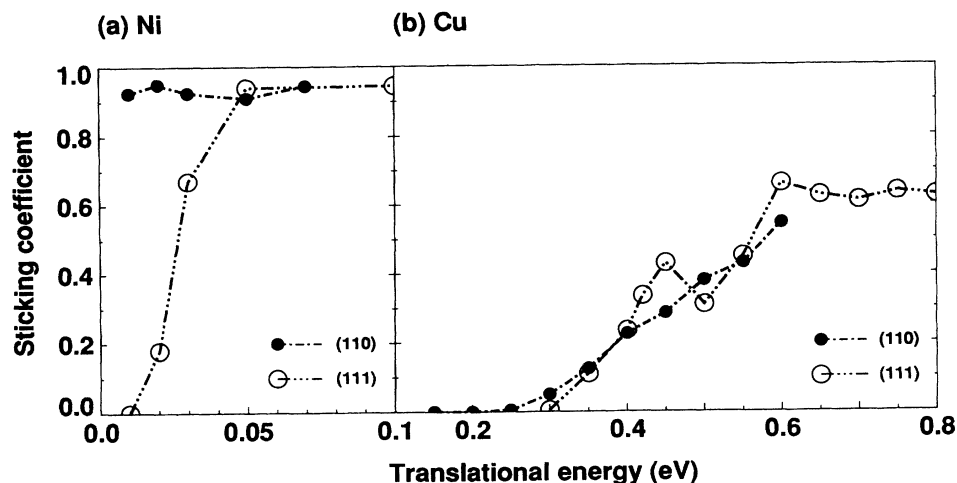


FIG. 3. The sticking probability of H_2 on the (111) and (110) surfaces of Cu and Ni calculated using a 6D quasi-classical simulation.

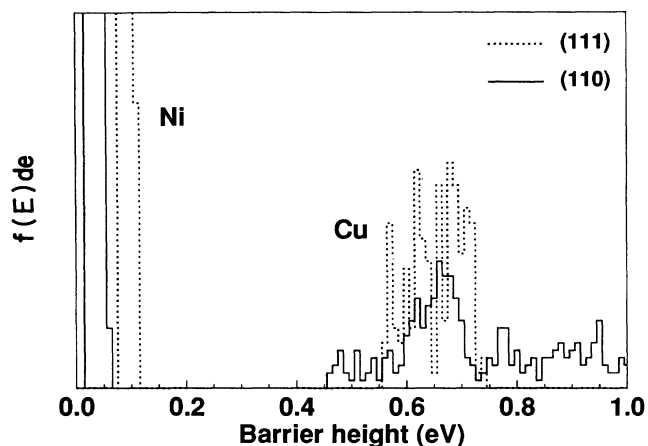


FIG. 4. Calculated distribution of activation energies for H_2 dissociation over the (111) and (110) faces of Cu and Ni. The distribution $f(E)dE$ is calculated as the fraction of the unit-cell area where a molecule impacting would experience a barrier between E and $E + dE$. Only impacts with the molecule lying flat on the surface are included, and the distribution is averaged with respect to the orientation of the molecular axis parallel to the surface (Ref. 18).

ing than those approaching the surface with substantial inclination.¹⁹ For Cu(111), however, this effect is more than compensated for in the threshold region by the possibility of out of plane motion when the dimensionality

is increased from 2 to 6.

All in all this means that the 6D Cu(111) results are not very different from the 2D ones, whereas on Cu(110) the difference is large, resulting in an accidental close similarity of the $S(E)$ curves for the two systems. On the Ni surfaces there is never a large difference between the 2D and 6D simulations because the barrier [for Ni(111)] is solely in the entrance channel, which means that dynamical effects are of minor importance on this metal.

In conclusion, the reactivity on the surface is dependent on the energetics and dynamics associated with the orientation of the molecule and the lateral impact point in a way and to a degree which is specific to the metal and crystal orientation. We are suggesting that for both Ni and Cu the open (110) surface has a minimum barrier for dissociation of H_2 which is considerably lower than for the close-packed (111) face. On Cu this is not observed in the measured energy dependence of the sticking probability due to dynamical effects including a large variation of the barrier with impact parameter on the open Cu(110) surface.

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¹³One of the basic ingredients in the potential construction

is the contribution of each atom to the electron density around another atom. The contribution of the H atoms to the electron density around the metal atoms are written $\Delta n_{am} = \Delta n_{0am} \exp(-\eta_{2am} r_{am})$, where r_{am} is the adsorbate-metal distance. The parameters η_{2am} and Δn_{0am} are calculated from the electron density of a H atom embedded in a homogeneous electron gas. In the present version we have (quite arbitrarily) changed Δn_{0am} from 0.001 19 to 0.000 25. This increases the barrier for dissociation of the molecule on the Cu surfaces substantially. For a detailed discussion of these points we refer to U. Nielsen and J. K. Nørskov (unpublished).

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¹⁸On the rough Cu(110) surface, the most favorable polar orientation of the impinging molecule, yielding the lowest barrier for given impact parameter, varies between approximately 60° and 120°, and the distribution depicted in Fig. 4 therefore overestimates the maximum barrier height encountered on Cu(110). The crucial point is, however, that the onset in the distribution at 0.46 eV — corresponding to the long-bridge-to-center dissociation geometry — remains valid, and that barrier heights in excess of 0.8 eV are found on this surface.

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